Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of the European Ceramic Society 24 (2004) 421–425

www.elsevier.com/locate/jeurceramsoc

Preparation of alkaline-earth metal silicates from gels and their NO_x-adsorption behavior

Shingo Katayama[a,*], Noriko Yamada[b], Masanobu Awano[c]

[a]Synergy Ceramics Lab., FCRA, Moriyama-ku, Nagoya 463-8687, Japan
[b]Nippon Steel Corporation, 20-1 Shintomi, Futtsu, Chiba 293-8511, Japan
[c]Synergy Materials R.C., AIST, Moriyama-ku, Nagoya 463-8687, Japan

Abstract

Processing of Ca and Ba silicates from gels was investigated aiming at the application to a NO_x absorbent. The gels were prepared from $R_nSi(OC_2H_5)_{4-n}$, $HSi(OC_2H_5)_3$ and alkaline-earth metals. Although alkaline-earth alkoxides readily react with water to give a precipitate, alkaline-earth metal was reacted with an alcohol solution of partially hydrolyzed $R_nSi(OC_2H_5)_{4-n}$ to give a stable mixture of alkaline-earth alkoxide and $R_nSi(OC_2H_5)_{4-n}$ in alcohol solvent. $HSi(OC_2H_5)_3$, which was used as a gelation acceleration agent, was added to the mixture. The solution was further hydrolyzed and allowed to gel at room temperature. The gels were transparent with no precipitation. The gels heat-treated at 600 °C were exposed to 1000 ppm NO diluted by Ar. FT-IR spectra of the Ca and Ba silicates showed the peaks corresponding to adsorbed NO species at the range of 1300–1600 cm^{-1}, whereas non-Ca, Ba silicate showed no FT-IR peaks corresponding to adsorbed NO species. Since more than one peak appeared in FT-IR spectrum of the NO-treated samples, it is likely that some types of NO_x adsorbate species exist on the surface of alkaline-earth silicates. It was known that the FT-IR peaks of adsorbed NO species disappeared at the heating temperature of 700 °C.

Keywords: Chemical properties; NO_x sorbent; Porosity; Silicates; Sol-gel processes

1. Introduction

The demands for the reduction of nitrogen oxides (NO_x) in emission from stationary and mobile sources have been increasing, which promotes not only a search for deNO_x catalysts[1] but also a development for electrochemical deNO_x cells using oxygen-conductive electrolyte.[2] Especially, the electrochemical cell with NO_x-selective electrode can reduce NO_x to N_2 without any reducing agents even in the presence of O_2.[3,4] At low temperatures, however, the reduction of NO_x is difficult for the electrochemical cell because of the low conductivity of oxygen ions in the electrolyte. In order to completely remove NO_x in low-temperature exhaust gas of engine starting, the electrochemical cell needs reversible sorbent of NO_x, which can absorb NO_x at low temperatures and release it at cell-working temperatures.

NO_x sorbent is well known in NO_x storage reduction catalysis, $Pt/BaO/Al_2O_3$, for cleaning automotive exhaust, in which NO_x gases are stored on the basic sites on Ba.[5] Also for the application to stationary emission sources, a similar reversible sorption–desorption operation has been investigated on a zirconia-based sorbent.[6] Some zirconia-based oxides also possess weak basicity to from stable nitrate on the surface and in the subsurface region. It is known that the NO_x-storing via the adsorption of NO_x by the acid-base interaction needs the solid-basic nature.

Silicates prepared by the sol-gel process are attractive for the NO_x sorbent because the sol-gel process provides porous bodies with a high surface area such as xerogels and aerogels, as well as meso- and micro-porous bodies derived from organic templates. Although pure silica is solid-acidic,[7] the incorporation of basic species such as alkali and alkaline-earth metal ions into silica networks can give a basic surface.[8,9] The authors have investigated sol-gel derived silicates with a solid-basic property aiming at the application to a NO_x absorbent combing with the electrochemical deNO_x cell with NO_x-selective electrode.

In the present paper, alkaline-earth metal silicates were synthesized from gels prepared from $R_nSi(OC_2H_5)_{4-n}$, $HSi(OC_2H_5)_3$ and alkaline-earth metals. The formation of silicates and their NO_x absorption–desorption behavior were investigated.

---

* Corresponding author.
E-mail address: shingo-katayama@aist.go.jp (S. Katayama).

0955-2219/03/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0955-2219(03)00211-5

2. Experimental procedure

Starting materials of silicates were tetraethoxysilane ($Si(OC_2H_5)_4$), methyltriethoxysilnae ($CH_3Si(OC_2H_5)_3$) and hydrido-triethoxysilane ($HSi(OC_2H_5)_3$), which were commercially available from Tokyo Kasei Kogyo Co., Ltd. Starting materials for alkaline-earth metal components were calcium metal and barium metal, which were commercially available from Wako Pure Chemical Industries Ltd. The preparation method of alkaline-earth metal silicates is shown in Fig. 1. $Si(OC_2H_5)_4$ or $CH_3Si(OC_2H_5)_3$ in $CH_3OC_2H_4OH$ was hydrolyzed with 1N HCl aqueous solution in a molar ratio of H_2O/-$OC_2H_5 = 0.5$. Ca or Ba metal was added into the hydrolyzed solution, followed by refluxing. Ca and Ba metals were reacted with an alcohol solution of the hydrolyzed $Si(OC_2H_5)_4$ and $CH_3Si(OC_2H_5)_3$ to give a stable mixture of alkaline-earth metal alkoxide and silicon alkoxide in alcohol solvent. $HSi(OC_2H_5)_3$, which was used as a gelation acceleration agent, was added to the mixture in the molar ratio of $HSi(OC_2H_5)_3$/$Si(OC_2H_5)_4$ or $CH_3Si(OC_2H_5)_3 = 1$. The solution was further hydrolyzed in the molar ration of H_2O/–$OC_2H_5 = 3$ and allowed to gel at room temperature. The molar ratio of alkaline-earth metal to total Si was 0.5. The gels were dried at 100 °C and heat-treated at 600 °C. The heat-treated gels were exposed to 1000 ppm NO diluted by Ar.

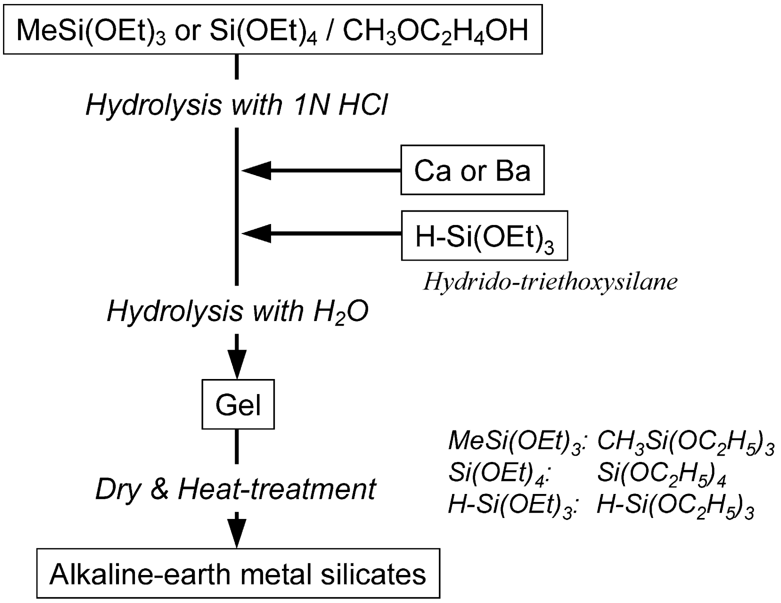

Fig. 1. Preparation method of alkaline-earth metal silicates.

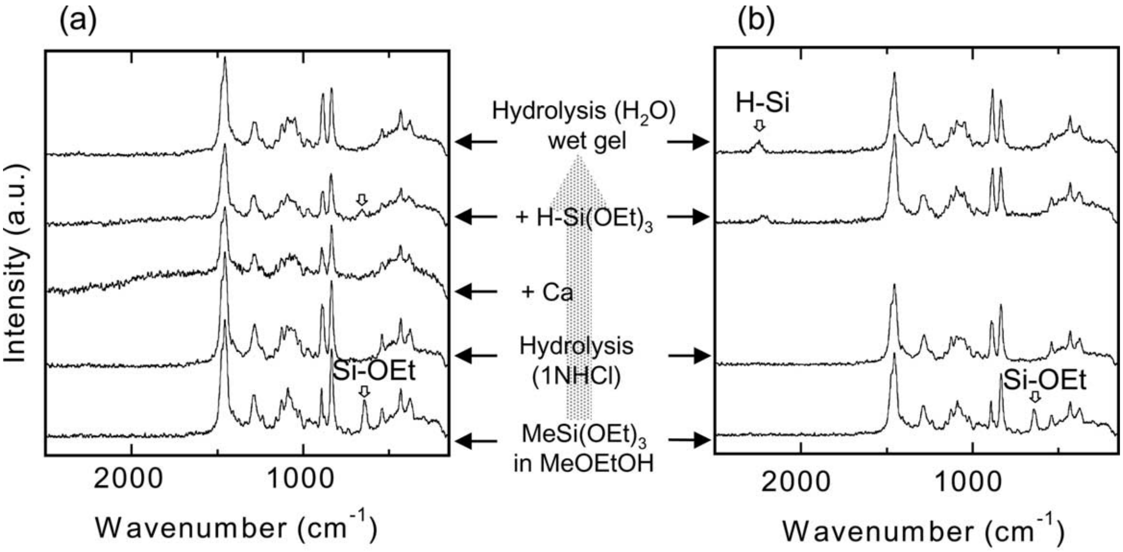

Fig. 2. FT-Raman spectra for (a) Ca silicate and (b) non-Ca silicate prepared from $CH_3Si(OC_2H_5)_3$ and $HSi(OC_2H_5)_3$.

FT-Raman spectra were recorded on a FT-Raman spectrometer of RFT-600, JASC Corp. with a YAG laser ($\lambda = 1060$ nm). The measurement of solid acid-base strengths was carried out with a series of Hammett indicators.[10] FT-IR spectra were recorded on a FT-IR spectrometer of Herschel FT/IR-610, JASC Corp. Samples were ground to a powder, which was measured by the KBr disk-method.

3. Results and discussion

FT-Raman spectra were measured from starting solutions to heat-treated gels for Ca and non-Ca silicates in order to investigate the reactions and formation behavior in this process. Fig. 2 shows the FT-Raman spectra for Ca and non-Ca silicates, which were prepared using $CH_3Si(OC_2H_5)_3$ and $HSi(OC_2H_5)_3$. In the FT-Raman spectrum of $CH_3Si(OC_2H_5)_3$ in $CH_3OC_2H_4OH$, the peak at 643 cm^{-1} was clearly observed, assigned to the $\nu(CSiO_3)$ stretching vibrations. This peak is known to diminish during hydrolysis, indicating the presence of unhydrolyzed $CH_3Si(OC_2H_5)_3$.[10] After the hydrolysis with 1N HCl, the peak at 643 cm^{-1} disappeared, meaning that $CH_3Si(OC_2H_5)_3$ was hydrolyzed. The peaks of ethanol that resulted from the hydrolysis of $CH_3Si(OC_2H_5)_3$ were not clearly recognized because their peaks overlapped with peaks of methoxyethanol solvent. When Ca metal was added into the hydrolyzed solution, it reacted with methoxyethanol solvent and/or hydrolyzed $CH_3Si(OC_2H_5)_3$ to yield a solution without precipitation. No clear difference between the FT-Raman spectra before and after adding Ca metal was observed. When $HSi(OC_2H_5)_3$ was furthermore added into the solution, some differences in FT-Raman spectra were observed. In the case of the Ca-added solution, the peak at 643 cm^{-1} appeared again but the peak of H–Si was not observed. This means that H–Si bonds of $HSi(OC_2H_5)_3$ were broken but ethoxy groups were not completely hydrolyzed. After the further hydrolysis with only water, the gelation occurred immediately as shown in Fig. 3. In the wet gel, the peak at 643 cm^{-1} also disappeared, meaning that the ethoxy groups were completely hydrolyzed. In the case of the solution not containing Ca, the peak at 643 cm^{-1} was not observed but the peak of H–Si was observed at 2240 cm^{-1}. This means that ethoxy groups of $HSi(OC_2H_5)_3$ were completely hydrolyzed but H–Si bonds were not broken. H–Si bonds are known to be stable in acidic condition but broken in basic condition.[11] It is understood that H-Si bonds are present in the non-Ca silicate because the hydrolysis is carried out with acidic water. In the wet gel of non-Ca silicate, the peak of H–Si at 2240 cm^{-1} was also observed, meaning the H–Si bonds

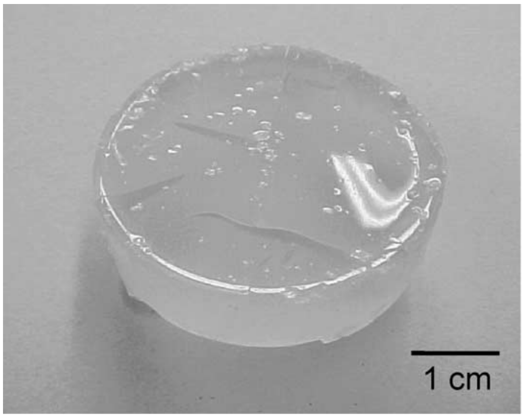

Fig. 3. Wet gel prepared from $CH_3Si(OC_2H_5)_3$, $HSi(OC_2H_5)_3$ and Ca.

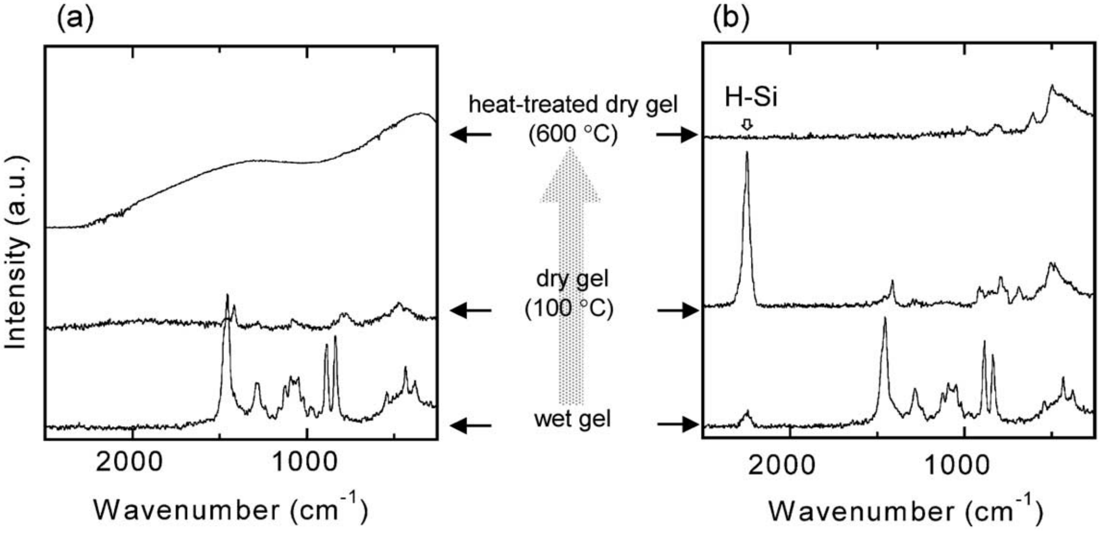

Fig. 4. FT-Raman spectra of wet gels, dried gels, and heat-treated gels for (a) Ca silicate and (b) non-Ca silicate prepared from $CH_3Si(OC_2H_5)_3$ and $HSi(OC_2H_5)_3$.

were present even in the gel. Fig. 4 shows FT-Raman spectra of wet gels, dried gels and heat-treated gels for Ca and non-Ca silicates. In the case of Ca silicate, the dried gel had Raman peaks corresponding to methyl groups derived from $CH_3Si(OC_2H_5)_3$ and the gel heat-treated at 600 °C showed that the Raman spectrum was changed from that of simple silica. In the case of non-Ca silicate, the dried gel had not only peaks corresponding to methyl groups derived from $CH_3Si(OC_2H_5)_3$ but also the peak of H–Si derived from $HSi(OC_2H_5)_3$. In the gel heat-treated at 600 °C, however, the peak of H–Si disappeared and the Raman spectrum resulted from typical silica, meaning the H–Si bonds were thermally broken by the heat-treatment.

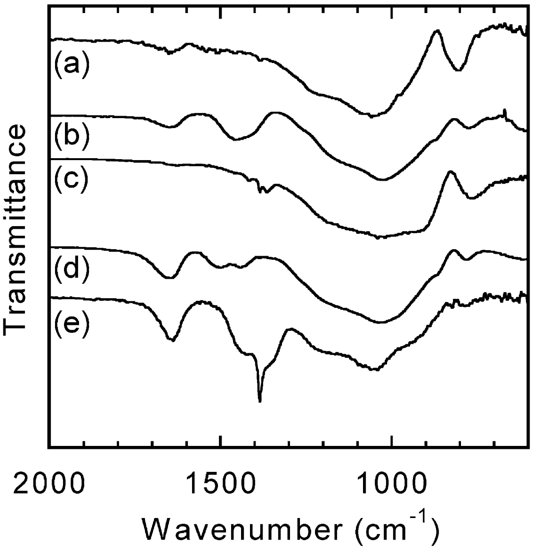

Fig. 5. FT-IR spectra of the gels heat-treated at 600 °C, which were exposed to 1000 ppm NO diluted by Ar. (a): non-Ca and Ba silicates, (b) Ca silicate prepared from $Si(OC_2H_5)_4$, (c) Ca silicate prepared from $CH_3Si(OC_2H_5)_3$, (d) Ba silicate prepared from $Si(OC_2H_5)_4$, Ba silicate prepared from $CH_3Si(OC_2H_5)_3$.

With regard to gels heat-treated at 600 °C, the solid acid-base strengths were measured with a series of Hammett indicators. Ca and Ba silicates showed the basic surface of $H_0 = 9$, whereas non-Ca, Ba silicate had the week acidic surface of $H_0 < 6.8$. The basicity of Ca and Ba silicates is thought to result from the incorporation of basic Ca and Ba components into siloxane networks. The basic surface is expected to effectively adsorb the acidic gases of NO_x.

Fig. 5 shows FT-IR spectra of the gels heat-treated at 600 °C, which were exposed to 1000 ppm NO diluted by Ar. In the case of Ca and Ba silicates, FT-IR peaks corresponding to adsorbed NO species appeared at the range of 1300–1600 cm^{-1}. Since non-Ca, Ba silicate, which indicated week acidic nature, showed no FT-IR peaks corresponding to adsorbed NO species, the basicity of Ca and Ba silicates is thought to govern the NO adsorption. In addition, since more than one peak appeared in the FT-IR spectrum of the NO-adsorbed silicates, it is likely that some types of NO adsorbate species exist on the surface of alkaline-earth silicates.[12,13]

The Ca and Ba silicates adsorbing NO were heated at various temperatures in air and measured by FT-IR as shown in Fig 6. Although the FT-IR peaks of adsorbed NO species was observed up to the heating temperature of 600 °C, they disappeared at the heating temperature of 700 °C.

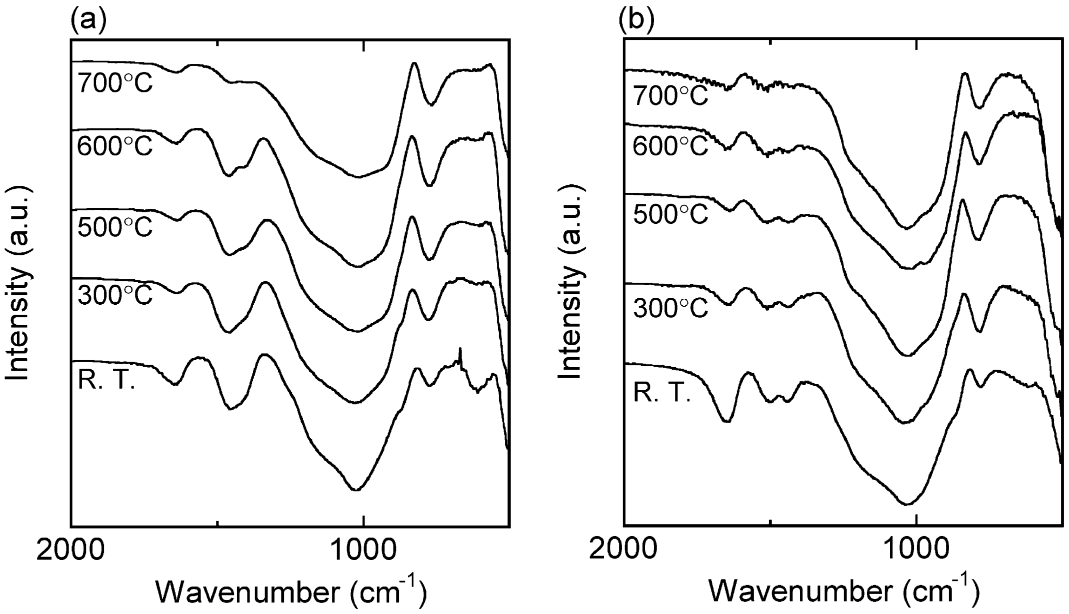

Fig. 6. FT-IR spectra of (a) Ca silicate and (b) Ba silicate exposed to 100 ppm NO diluted by Ar and NO-adsorbing silicates heated at various temperatures in air.

4. Conclusions

The alkaline-earth metal silicates were prepared from gels obtained by the sol-gel process using $R_nSi(OC_2H_5)_{4-n}$, $HSi(OC_2H_5)_3$ and alkaline-earth metals as starting materials. By FT-Raman measurements, it was found that ethoxy groups of $R_nSi(OC_2H_5)_{4-n}$ and $HSi(OC_2H_5)_3$ were hydrolyzed and H–Si bonds of $HSi(OC_2H_5)_3$ were broken during the process from starting solution to gel. The Ca and Ba silicates prepared by heat-treatment of the gels at 600 °C were found to adsorb NO. The adsorbed NO species were released at the heating temperature of 700 °C.

Acknowledgements

This work has been supported by NEDO, as part of the Synergy Ceramics Project promoted by METI, Japan. The authors are members of the Joint Research Consortium of Synergy Ceramics.

References

1. Garin, F., *Appl. Catal. A: General*, 2001, **222**, 183–219.
2. Hibino, T., Chem. Lett. 1994 927–930.
3. Bredikhin, S., Maeda, K. and Awano, M., *J. Electrochem. Soc.*, 2001, **148**, D133–D138.
4. Bredikhin, S., Matsuda, K., Maeda, K. and Awano, M., *Solid State Inonics*, 2002, **149**, 327–333.
5. Fridell, E., Persson, H., Westerberg, B., Olsson, L. and Skoglundh, M., *Catal. Lett.*, 2000, **66**, 71–74.
6. Matzukuma, L., Kikuyama, S., Kikuchi, R., Sasaki, K. and Eguchi, K., *Appl. Catal. B. Enviromental*, 2002, **73**, 107–115.
7. Tanabe, K., Misono, M., Ono, Y. and Hattori, H., *New Solid Acids and Bases, their Catalytic Properties*. Elsevier, Amsterdam, 1989.
8. Tanabe, K., Misono, M., Ono, Y. and Hattori, H., *New Solid Acids and Bases, their Catalytic Properties*. Elsevier, Amsterdam, 1989.
9. Katayama, S., Iwata, K., Kubo, Y. and Yamada, N., *J. Sol-Gel Sci. Tech.*, 2002, **26**, 1–5.
10. Tanabe, K., Misono, M., Ono, Y. and Hattori, H., *New Solid Acids and Bases, their Catalytic Properties*. Elsevier, Amsterdam, 1989.
11. Belot, V., Corriu, R., Leclecq, D., Lefevre, P., Mutin, P. H., Vioux, A., and Flanck, A. M., In *Chemical Processing of Advanced Materials*. ed. L. L. Hench and J. K. West., John Wiley and Sons, New York, 1992 pp. 143–158.
12. Low, M. J. and Yang, R. T., *J. Catal.*, 1974, **43**, 479–489.
13. Chi, Y. and Chaung, S. C., *J. Catal.*, 2000, **150**, 75–91.